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Gold(I) Complexes with "Normal" 1,2,3-Triazolylidene Ligands: Synthesis and Catalytic Properties

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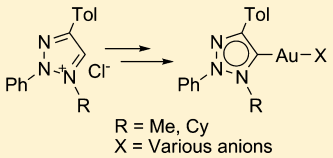
Supporting Information

ABSTRACT: 1,2,3-Triazolylidenes as versatile, strong donor ligands have currently experienced a boost in complex synthesis as well as catalytic applications. Although many examples of "abnormal" 1,2,3-triazolylidenes have been described, their "normal" congeners have been barely examined to date (for abnormal carbenes the resonance structures of the carbenes cannot be drawn without adding additional charges, but this is possible for normal carbenes). Furthermore, no instance of utilization of this new ligand class in homogeneous catalysis can be found. Therefore, this work presents a variety of potential precatalysts descending from "normal" 1,2,3-triazolylidene Au chloride complexes. Synthesis and thorough characterization of the new compounds are presented, together with special ligand features such as buried volume and suspected anagostic interactions. The activity of the isolated precatalysts is examined in the intramolecular hydroamination of alkynes and compared with that of a popular imidazolylidene system. It is found that the activity of the best-performing "normal" 1,2,3-triazolylidene systems is quite similar to that of the imidazolylidene systems. However, mercury drop poisoning experiments suggest that improvements in ligand design are required to enhance catalyst stability.



INTRODUCTION

Ever since the potential of N-heterocyclic carbenes (NHCs) as versatile, tailor-made ligands for organometallic catalysts was discovered,[1] this research area has experienced an enormous boost.[2] Due to their almost unparalleled versatility, NHCs are nearly ubiquitous in organometallic research and applications today.[3] In addition to "normal" imidazoleylidenes, an entire range of different N-heterocyclic carbenes with varying substitution patterns is available.[4] Nevertheless, it took more than 30 years since the early beginnings of NHCs[5] until the first abnormal coordinated carbenes were described.[6] Soon after, the strong σ-donor properties of abnormally bound imidazolylidenes were discovered and interest rose in this research area.[7] With the isolation of the first 1,2,3-triazolylidene ligands coordinated to transition metals,[8] the definition of abnormal binding carbenes was widened (Figure 1): for a normal NHC, the free carbene structure can be drawn without additional charge, while a graphical representation of free abnormal carbenes requires the indication of charges.[9]

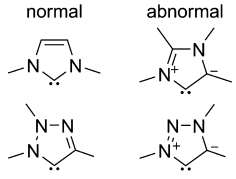


Figure 1. Graphical representation of free carbene structures for normal and abnormal imidazolylidenes as well as normal and abnormal triazolylidenes.

Since access to variously substituted 1,2,3-triazolium salts as precursors for abnormal triazolylidenes is straightforward and due to their elevated σ-donor strength, numerous reports of varied ligand systems[10] and their catalytic application[11] have emerged. Recently we have shown that access to "normal" 1,2,3-triazolylidene ligands is possible by changing the 1,3,4-substitution in abnormal 1,2,3-triazolylidenes to a 1,2,4-substitution pattern.[12]

During the past decade, scientific interest in homogeneous Au-catalyzed organic transformations (i.e., hydration, hydroalkoxylation, or hydroamination of alkenes or allenes, enyne cyclizations) has experienced steep growth.[13] After the first reports of the synthesis and preliminary application of NHC Au compounds,[14] this field quickly widened for this ligand class.[15a−d] Even Au complexes with abnormal saturated imidazolylidenes have been synthesized.[15e,f] Furthermore, abnormal triazolylidene compounds were isolated and preliminarily tested in catalytic applications.[11c] In order to examine the viability of the new ligand system of normal triazolylidenes and inspired by the wide variety of potential applications available for NHC Au compounds, in this paper we have synthesized a series of Au complexes coordinated with normal 1,2,3-triazolylidene ligands and examined their feasibility in catalysis.

RESULTS AND DISCUSSION

Complex Synthesis and Characterization. For metal complex synthesis, methyl- and cyclohexyl-substituted normal

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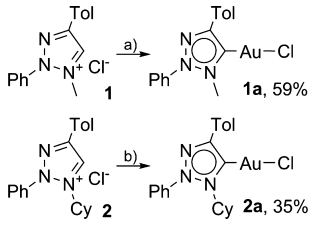
triazolium chlorides were selected as precursors. They were prepared according to routes described earlier by Moderhack and co-workers, providing access a large variety of these salts.[16] After the successful synthesis of Rh and Ir complexes by applying an *in situ* silver carbene generation reaction protocol,[12] the corresponding Au compounds were prepared analogously (Scheme 1). Isolation of the methyl triazolylidene Au−Cl

Scheme 1. Synthesis of Triazolylidene Au−Cl Complexes Starting from Triazolium Chlorides[a]



[a]Reaction conditions: (a) 1 0.50 equiv of Ag_2O, room temperature, exclusion of light, 2 h, CH_2Cl_2, 2 0.90 equiv of [$AuCl(SMe_2)$], room temperature, exclusion of light, 2 h, CH_2Cl_2; (b) 1 1.50 equiv of Ag_2O, molecular sieves, room temperature, exclusion of light, 18 h, MeCN/CH_2Cl_2 1/1, 2 0.90 equiv of [$AuCl(SMe_2)$], room temperature, 2 h, CH_2Cl_2.

compound **1a** was confirmed by comparing ^{1}H and ^{13}C NMR values with previously published data.[12] Note that for the synthesis of complex **2a** with cyclohexyl-substituted triazolylidene different reaction conditions had to be applied. A MeCN/CH_2Cl_2 1/1 solvent mixture only proved adequate for in situ silver carbene generation. However, yields were unsatisfying in this case (35%) and could not be further improved—despite numerous attempts—by applying diverging reaction conditions. As soon as the cyclohexyl-substituted carbene is bound to the Au metal center, however, high complex stability of **2a** is observed, as the compound can even be purified by column chromatography under aerobic conditions. Formation of **2a** was first confirmed by means of ^{1}H NMR, since the proton bound to the *ipso* carbon atom of the cyclohexyl ligand proved to be a viable indicator for metal complexation. A shift for this characteristic triplet of triplets from the triazolium salt (4.52 ppm in $CDCl_3$) to the Au compound (4.40 ppm in $CDCl_3$) could be monitored. Furthermore, the vanishing of the characteristic triazolium proton signal (11.84 ppm in $CDCl_3$) suggests metal coordination. ^{13}C NMR gives further evidence for metal complexation, since a resonance for the carbene carbon can be identified at 158.2 ppm, which is, however, a surprisingly low value in comparison to those for similar imidazolylidene-based compounds.[14b] Nevertheless, it corresponds well with observations made by Crowley et al.[11c] for abnormal triazolylidene Au compounds.

In addition to the NMR data (vide supra), mass spectroscopy was necessary to prove the generation of an Au compound instead of an Ag complex. ESI-MS and FAB-MS prove useful for this purpose and give several mass peaks suggesting Au carbene complexation (513.5 $[M - Cl]^+$, 1061.3 $[2M - Cl]^+$, 413.5 $[M - Cy - Cl]^+$ for ESI; 513.5 $[M - Cl]^+$ for FAB). The observed mass peaks, corresponding to a bis(triazolylidene) compound, are probably created under ESI conditions, since single-crystal X-ray spectroscopy of **2a** (Figure 2)—grown by slow evaporation of the solvent from a saturated solution of **2a** in dichloromethane—implies that the mono(triazolylidene) Au−Cl complex is the preferred species at room temperature.

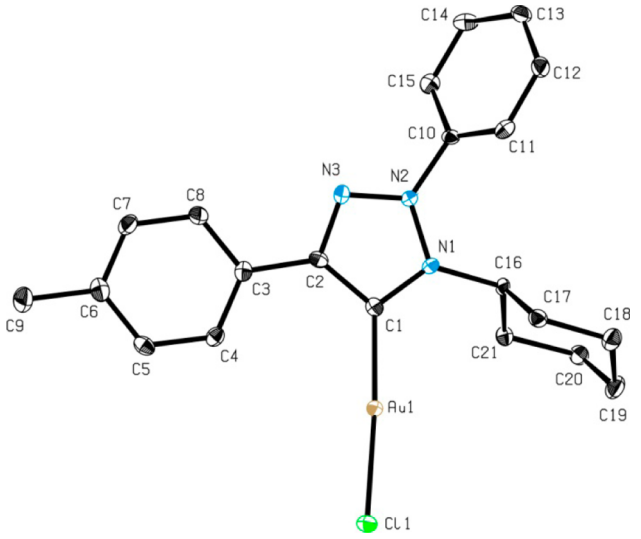


Figure 2. Molecular structure for **2a**, obtained from X-ray crystallographic data (thermal ellipsoids are shown at a probability level of 50%). Selected bond distances (Å), angles (deg) and torsion angles (deg): Au1−C1 = 1.989(3), Au1−Cl1 = 2.2898(6), H4···Au1 = 2.6030(2), H21a···Au1 = 2.7302(2), H17b···Au1 = 2.9254(2); Cl1−Au1−C1 = 174.98(7), Au1−H4−C4 = 141.0(2), Au1−H21a−C21 = 134.1(1), Au1−H17b−C17 = 130.6(2); N3−N2−N1−C16 = 169.1(2).

Furthermore, elemental analysis additionally supports the isolation of **2a**.

The crystal structure of **2a** can be compared to the earlier published structure of **1a**.[12] The carbene−metal distance in **2a**, Au1−C1 = 1.989(3) Å, is similar to the bond distance observed in **1a** (1.997(6) Å); the same is true for the Au1−Cl1 distance (2.290(1) Å), which is 2.290(2) Å in **1a**. A somewhat larger variation is detected when the Cl1−Au−C1 angles (**2a**, 174.98(7)°; **1a**, 177.13(15)°) or the torsion angles are compared (N3−N2−N1−C16: 176.4(5)° in **1a** and 169.1(2)° in **2a**). These slight differences might be attributed to the increased steric demand of the cyclohexyl ligand. Interestingly, the structure of **2a** shows a weak interaction between the Au center and one proton of the triazolylidene's tolyl group, evidenced by the short H4···Au1 distance of 2.6030(2) Å. This interaction might be responsible for the unusual upright position of the tolyl group, which is positioned parallel to the ligand's plane. A similar interaction with the metal center can be observed for one proton of the triazolylidene's cyclohexyl group (H21a···Au1 = 2.7302(2) Å). Both interactions can be described as anagostic interactions.[17] This observation correlates well with the downfield-shifted ^{1}H NMR signal of the ortho proton of the tolyl group (8.26 ppm in **1a** and 8.33 ppm in **2a**). However, the integral of this signal corresponds to two protons, suggesting that the proton−Au interaction is too weak to prevent rotation of the tolyl group. Even in variable-temperature (VT) ^{1}H NMR studies the assumed rotation cannot be stopped at −87 °C. In order to gain further insight into the nature of the Au···H interactions and possible energetic benefits associated with these, the optimized structure of **1a** without protons—to exclude any influence of a proton−metal interaction—has been calculated. Interestingly, the optimized structure shows a very similar position of the tolyl group relative to the heterocycle's plane (torsion angle C1−C2−C3−C4 −8(1)° vs 16.02° in the calculated structure; see the Supporting Information for further

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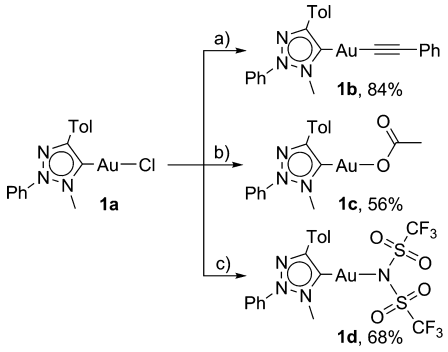
details). Accordingly, it is possible to consider the observed anagostic interaction as negligible, while the position of the tolyl group may simply be explained through a π interaction of the aromatic systems of the tolyl group and triazolylidene.

For complete characterization the buried volumes of the two new triazolylidene ligands were calculated by uploading the modified CIF files of **1a** and **2a** in the SambVca web application provided by Cavallo and co-workers.[18] Nolan et al.[19] provided a series of buried volumes calculated for NHC ligands obtained from the corresponding [AuCl(NHC)] complexes. The parameters utilized by this group were also used for our calculations to allow for better comparison (see the Supporting Information for further details). For the carbene ligand derived from **1**, buried volumes of 29.0% (2.00 Å M−$C_{carbene}$ distance) and 25.3% (2.28 Å M−$C_{carbene}$ distance) were obtained, whereas the carbene ligand derived from **2** gave buried volumes of 34.8% (2.00 Å M−$C_{carbene}$ distance) and 30.6% (2.28 Å M−$C_{carbene}$ distance). Accordingly, the buried volume of the carbene ligand derived from **1** is slightly higher than that of ICy (27.4% (2.00 Å); 23.5% (2.28 Å)) and the V_{bur} value of the carbene ligand derived from **2** is somewhat smaller than that of IMes (36.5% (2.00 Å); 31.2% (2.28 Å)).[19]

In the search for viable triazolylidene Au precatalysts, a series of halide substitution reactions starting from the methyl-substituted triazolylidene Au chloride complex **1a** has been tested. Different Au compounds with a variety of ligands were synthesized in order to avoid the use of Ag salts for halide dissociation during catalysis, as the catalytic results may be influenced.[20] First of all, the synthesis of a phenylacetylide congener was attempted,[21] reported earlier for an abnormal triazolylidene-substituted Au compound by Lee and Crowley.[11c] The reaction was straightforward and led to the formation of the phenylacetylide-substituted, air- and moisture-stable Au compound **1b** in good yields (Scheme 2).

Scheme 2. Syntheses of Various Au Precatalysts[a]



[a]Reaction conditions: (a) solution (made from stirring 2.10 equiv of KO^{t}Bu and 2.10 equiv of phenylacetylene in MeOH for 20 min at room temperature) added, room temperature, 12 h, MeOH; (b) 1.20 equiv of AgOAc, −78 °C to room temperature, 16 h, CH_2Cl_2; (c) 1.05 equiv of $AgN(Tf)_2$, room temperature, 5 min, CH_2Cl_2.

Isolation of **1b** was confirmed via ^{1}H (shift of NMe singlet from 4.22 ppm of **1a** in CD_2Cl_2 to 4.27 ppm of **1b** in $CDCl_3$, shift of tolyl doublet from 8.26 ppm in CD_2Cl_2 to 8.33 ppm in $CDCl_3$, appearance of additional Ph signals) and ^{13}C NMR (characteristic carbene signal shifted to 180.1 ppm in $CDCl_3$ for **1b** from 163.4 ppm in CD_2Cl_2 for **1a**). Compound **1b** was further characterized by ESI-MS, FAB-MS, and elemental analysis (see the Experimental Section). Single crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a solution of **1b** in chloroform. Unfortunately, data were insufficient for full structural characterization and solely allowed for structural confirmation (see the ball-and-stick representation in the Supporting Information).

Compound **1c** was synthesized according to a procedure reported earlier,[14a] describing the synthesis of the first NHC Au acetate complex. For the generation of complex **1c**, silver acetate is added to the reaction mixture at −78 °C. Although immediate precipitation of silver chloride could be observed, the reaction mixture was stirred overnight at room temperature to ensure full conversion. ^{1}H NMR spectroscopy gave rise to a new distinctive signal for the acetate ligand's methyl group at 1.96 ppm in CD_2Cl_2. Furthermore, ^{13}C NMR revealed a downfield-shifted carbene signal at 176.9 ppm in CD_2Cl_2. In addition to full characterization (see the Experimental Section for details), single crystals of **1c** were grown by recrystallization in MeCN. Figure 3 provides an ORTEP-style representation of

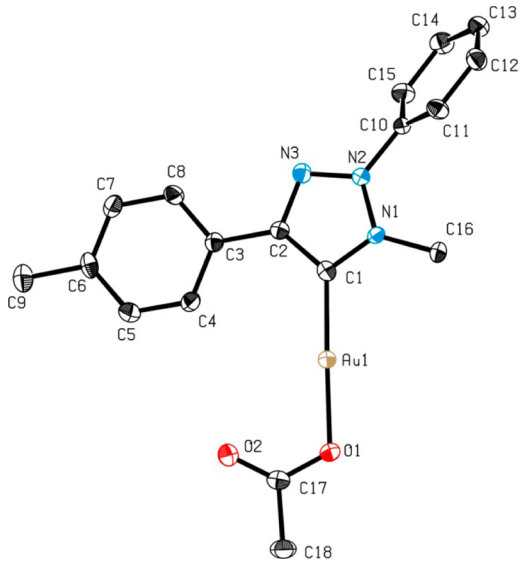


Figure 3. Molecular structure for **1c**, obtained from X-ray crystallographic data (thermal ellipsoids are shown at a probability level of 50%). Selected bond distances (Å) and angles (deg): Au1−C1 = 1.970(3), Au1−O1 = 2.046(2), O1−C17 = 1.285(4), O2−C17 = 1.230(4), H4···Au1 = 2.5850(1); O1−Au1−C1 = 176.5(1).

the solid-state structure of compound **1c**. The crystal structure confirms the linear coordination with an O1−Au1−C1 angle of 176.5(1)°, close to the observations made for the related compounds [Au(IPr)(OAc)] first presented by Nolan et al.[22] (two molecules in the asymmetric unit: angles 171.6(6)° and 179.3(6)°) and the NHC Au acetate compound synthesized by Herrmann and co-workers (179.3(2)°).[14a] The angle is very close to the P−Au−O angle in [Au(OAc)(PPh_3)] (177.3(2)°).[23] The carbene carbon−Au bond length in **1c** (1.970(3) Å) is similar (within the limits of triple standard deviation) to that of the compound previously described by Herrmann et al.[14a] (1.961(5) Å) and is between the bond lengths observed for the two molecules of the IPr congener (1.98(1) and 1.95(2) Å).[23] The double-bond character of O2−C17 is evident from the shortened bond length of 1.230(4) Å in comparison to O1−C17 (1.285(4) Å). Just as in the crystal structures of **1a**[12] and **2a**, an anagostic interaction between H4

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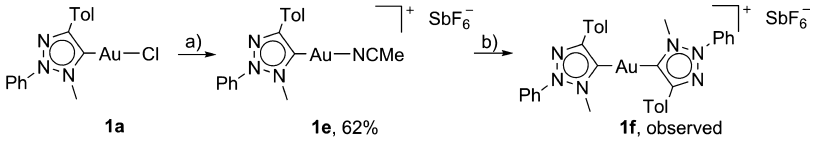
Scheme 3. Synthesis of Acetonitrile-Coordinated Au Precatalyst 1e and Observed Bis(triazolylidene) Compound Formation[a]



[a]Reaction conditions: (a) 1.05 equiv of $AgSbF_6$, room temperature, 1 min, MeCN; (b) room temperature, weeks, $MeCN/Et_2O$.

and the Au center can be observed in **1c** (H4···Au1 = 2.5850(1) Å).

Since silver bis(trifluoromethanesulfonyl)imide ($Ag(NTf_2)$) is commonly used in Au-catalyzed organic transformations, we decided to synthesize a well-defined triazolylidene Au precatalyst with NTf_2^- as the anion. For the synthesis of compound **1d** (Scheme 2), an procedure reported earlier for $[Au(NHC)(NTf_2)]$ compounds, described by Gagosz and co-workers, was applied.[24] Also for the normal triazolylidene congener, the reaction proceeds smoothly and is complete after 5 min. The carbene carbon resonance shows an upfield shift in ^{13}C NMR, namely from 163.4 ppm (CD_2Cl_2) in **1a** to 156.1 ppm (CD_2Cl_2) in **1d**, which is in accordance with the reported shift of $[Au(IPr)(NTf_2)]$ (168.3 ppm in CD_2Cl_2)[24] from [AuCl(IPr)] (175.1 ppm in CD_2Cl_2).[14b] In addition, the characteristic quartet for the NTf_2^- trifluoromethyl group can be found at 120.0 ppm ($^1J_{CF}$ = 323.0 Hz).

The transformations presented above describe reactions to substitute the Cl^- anion in **1a** by other anions, more or less strongly bound to the metal center. However, halide replacement by a weakly coordinating anion (WCA) seems even more promising for possible catalytic applications.[25] For this reason, a series of exchange experiments were executed, applying Ag salts of WCAs such as PF_6^-, BF_4^-, and SbF_6^-. In the case of PF_6^- and BF_4^-, no clean product formation could be observed. ^{19}F NMR revealed not only the multiplets typical for these anions but also resonances of suspected P–F or B–F bond activation products, as already observed by other groups.[14c,26] The use of SbF_6^- helps to avoid such side products and allows for clean isolation of the acetonitrile-coordinated compound **1e** (Scheme 3).

As mentioned by Nolan et al.,[14c] only very short reaction times followed by immediate filtration and evaporation of the reaction solution prevents partial formation of a presumed bis(carbene) side product. Complex **1e** could be isolated as a white powder, displaying high stability in the solid state when stored under argon and limited stability when kept in solution for 24 h at room temperature. Despite its limited stability in solution, complete characterization could be carried out successfully. ^1H NMR spectroscopy measured in CD_2Cl_2 suggests acetonitrile coordination, due to an additional methyl group observable at 2.49 ppm. In the ^{13}C NMR, a typical upfield-shifted carbene carbon resonance can be identified at 156.6 ppm. In ESI-MS the Au acetonitrile cation can be found ($[M - SbF_6]^+$ 487.1) and FAB-MS gives mass peaks for $[M - SbF_6]^+$ and $[M - SbF_6 - MeCN]^+$ as well as for the bis(triazolylidene) Au compound. The presence of coordinated acetonitrile could be unequivocally proven by elemental analysis. This finding is of particular importance, because an analysis of crystals of **1e** presumed to be suitable for X-ray diffraction only gave the structure of the related bis-(triazolylidene) complex **1f** (Figure 4). In another set of crystals, the same structural information was found. This allows us to conclude that the complex stability is limited in solution at

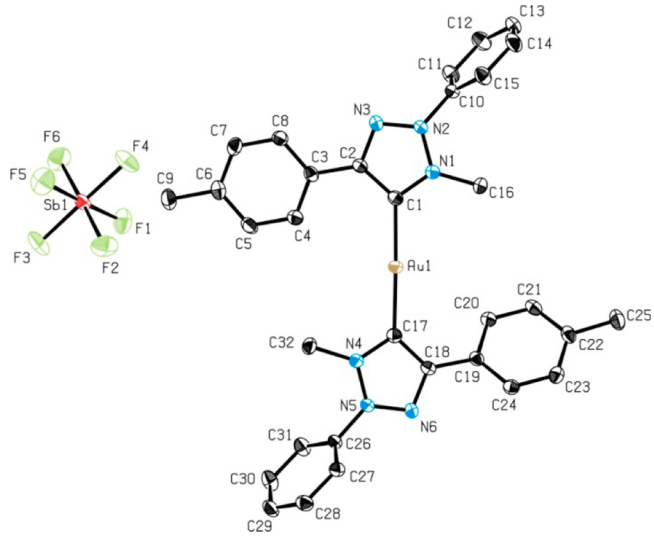


Figure 4. Molecular structure for **1f**, obtained from X-ray crystallographic data (thermal ellipsoids are shown at a probability level of 50%). Selected bond distances (Å), angles (deg), and torsion angles (deg): Au1–C1 = 2.031(2), Au1–C17 = 2.026(2), N1–N2 = 1.365(3), H4···Au1 = 2.5300(2), H20···Au1 = 2.8487(2); C1–Au1–C17 = 177.05(9), N1–C1–C2 = 103.2(2); N3–N2–N1–C16 = 176.8(2), C4–C3–C2–C1 = −7.9(4), C20–C19–C18–C17 = −33.3(3).

room temperature and leads to decomposition and partial bis(carbene) formation. However, upon heating in CD_3CN or CD_2Cl_2 for days, we were not able to isolate this bis(carbene) species without side products.

The crystal structure of this Au bis(triazolylidene) complex **1f** reveals an almost ideal linear coordination of two normal triazolylidene ligands (C1–Au1–C17 = 177.05(9)°). In the crystal structure of the complex $[Au(NHC)_2]PF_6$, described by Meyer and co-workers,[27] this angle is almost the same (C1–Au1–C31 = 177.07(13)°). Au–carbene bond lengths, however, are slightly elongated in the bis(triazolylidene) complex (Au1–C1 = 2.031(2) Å, Au1–C17 = 2.026(2) Å) in comparison with Meyer's bis(NHC) compound (Au1–C1 = 2.015(3) Å, Au1–C31 = 2.018(3) Å). This observed bis(triazolylidene) formation represents a possible resting state of any of the synthesized Au precatalysts in any desired catalytic cycle and may prove to be an impediment for catalyst performance due to its presumed stability. As in the other structures, a slight anagostic interaction can be observed between the *ortho* proton of the tolyl ligand and the metal center (H4···Au1 = 2.5300(2) Å). However, in this example one tolyl ring is further twisted relative to the triazolylidene plane (C17–C18–C19–C20 −33.4(3)°), certainly due to steric restrictions.

Nevertheless, apart from the observed slow bis(carbene) formation behavior in solution, compound **1e** seems most promising for applications, due to its rather labile acetonitrile substituent. Hence, the cyclohexyl-substituted acetonitrile-

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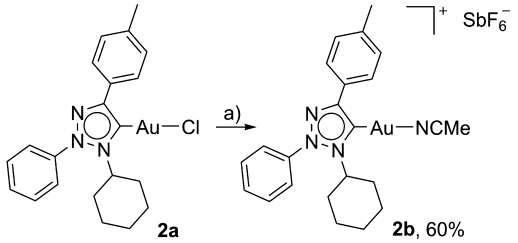
coordinated complex **2b** was synthesized by following the reaction protocol applied above (Scheme 4). When performed as an NMR experiment, quantitative formation of **2b** can be observed within minutes. Therefore, no prolonged reaction time is necessary. When it is measured in CD_2Cl_2, the typical methyl group representing the coordinated acetonitrile can be observed at 2.52 ppm. The downfield-shifted signal of the carbene carbon at 157.3 ppm in ^{13}C NMR gives further evidence for successful halide replacement.

Scheme 4. Synthesis of Acetonitrile-Coordinated Precatalyst 2b[a]



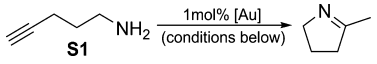
[a]Reaction conditions: (a) 1.05 equiv of $AgSbF_6$, room temperature, 5 min, MeCN.

These syntheses prove that viable Au precatalysts coordinated by normal 1,2,3-triazolylidenes can be easily prepared in good yields using standard reagents. Compounds **1a**,**b** and **2a** are air- and moisture-stable, as observed in water-containing NMR solvents over several days. Compounds **1c**−**e** are air- and moisture-stable for hours in the solid form but have to be stored under argon. Furthermore, the compounds were observed to be temporarily stable in water-containing NMR solvents. However, within 1 day formation of a deep red solution is observable, which can be ascribed to complex decomposition and formation of colloidal Au nanoparticles. Complex **2b** appears to be less stable, and partial decomposition could be monitored within hours in NMR solvents containing only traces of moisture.

Catalytic Application in Hydroamination. All synthesized compounds were applied as catalysts in the hydroamination of 4-pentyn-1-amine, yielding a ring-closing product (Table 1), as recently shown for NHC Cu complexes.[28] For comparison of catalysts **1a**−**e** and **2a**,**b**, very mild reaction conditions (34 °C, 24 h) were applied. Although this reaction is also catalyzed at room temperature by some of the Au compounds, this slightly elevated reaction temperature was used in order to maintain the exact same conditions for all catalytic tests. Since in this transformation no side products are observed, yields can be monitored via ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

When the catalyst screening was performed, phenylacetylide-substituted precatalyst **1b** turned out to be the least active catalyst, followed by the chloride-substituted complex **2a**, acetate-substituted congener **1c** and chloride-substituted complex **1a**. Better-performing precatalysts contained more labile substituents, such as acetonitrile (**1e**, **2b**) and NTf_2^- (**1d**). In order to further compare the new 1,2,3-triazolylidene compounds with more established catalytic systems, [Au(IPr)(NCMe)]BF_4 was applied as a precatalyst under the same reaction conditions. Yields were found to be only slightly higher in comparison to the most active normal 1,2,3-triazolylidene compounds (Table 1; entries 3, 7, 8, and 10). However, minor formation of Au colloids can be observed in the case of complexes **1e** and **2b**, while no Au colloids are observable under the tested reaction conditions when using **1d** or [Au(IPr)(NCMe)]BF_4. These two complexes were also tested at room temperature (Table 1, entries 19 and 20) and showed mediocre activity. In order to examine whether carbene ligands were necessary or whether Au nanoparticles catalyze the reaction, the Au precursor [$AuCl(SMe_2)$] was applied as catalyst. Immediately, a black precipitate immediately formed even at room temperature, while higher yields were obtained (97%).

Table 1. Overview of Catalytic Examinations of Catalysts 1a−e and 2a,b in the Intramolecular Hydroamination of Alkyne-Amine S1



entry[a]	catalyst	solvent	temp (°C)	time (h)	yield (%)[b]
1		CD_2Cl_2	34[c]	24	0[e]
2	[$AuCl(SMe_2)$]	CD_2Cl_2	34[c]	24	97[d]
3	[Au(IPr)(NCMe)]BF_4	CD_2Cl_2	34[c]	24	84[d]
4	**1a**	CD_2Cl_2	34[c]	24	39[d]
5	**1b**	CD_2Cl_2	34[c]	24	11[d]
6	**1c**	CD_2Cl_2	34[c]	24	24[d]
7	**1d**	CD_2Cl_2	34[c]	24	75[d]
8	**1e**	CD_2Cl_2	34[c]	24	77[d]
9	**2a**	CD_2Cl_2	34[c]	24	23[d]
10	**2b**	CD_2Cl_2	34[c]	24	77[d]
11	**1d**	toluene	34[c]	24	18[e]
12	**1d**	toluene	85[c]	24	70[e]
13	**1d**	DMSO	34[c]	24	9[e]
14	**1d**	THF	34[c]	24	27[e]
15	**1d**	CD_3CN	34[c]	24	53[e]
16	**1d**	CD_3CN	80[c]	2	67[e]
17	**1d**	CD_3CN	80[c]	14	89[e]
18	**1d**	CD_3CN	80[c]	21	96[e]
19	**1d**	CD_2Cl_2	24[c]	24	43[e]
20	[Au(IPr)(NCMe)]BF_4	CD_2Cl_2	24[c]	24	63[e]

[a]Catalytic reactions were performed in J. Young NMR tubes, using 0.138 mmol of **S1** and 1.38 μmol of catalyst (see the Experimental Section), with 1,3,5-trimethoxybenzene as internal standard in 0.6 mL of deuterated solvent. [b]Determined by NMR. [c]±1 °C. [d]Average of three runs. [e]Average of two runs.

Since the most stable 1,2,3-triazolylidene precatalyst seems to be NTf_2^--substituted **1d**, this compound was examined under varied reaction conditions (Table 1, entries 11−18). At 34 °C, **1d** catalyzes the ring-closing hydroamination reaction of **S1** best in CD_2Cl_2, followed by acetonitrile. At elevated temperatures, the reaction is best catalyzed in MeCN, leading to satisfactory yields (89%) within 14 h: however, not without slightly visible Au colloid formation. Under these conditions, kinetic measurements of the reaction were undertaken (Figure 5).

From the kinetic examination, a turnover frequency of 76 h^{-1} can be deduced. However, conversion strongly drops after the first few hours and reaction is not complete even after 27 h. In view of the fact that high yields were readily obtained with **1d** at 34 °C within 24 h (Table 1, entry 7), the yields obtained at 80 °C give reason to question the catalyst stability under these conditions. Therefore, poisoning experiments were undertaken by adding mercury to the reaction solution (refer to Supporting

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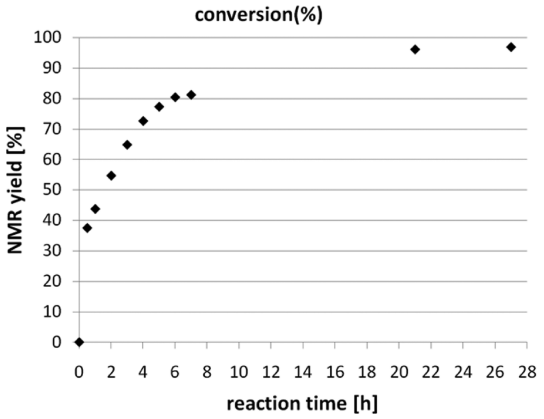
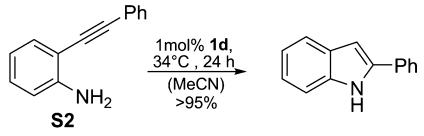


Figure 5. Kinetic examination of the intramolecular hydroamination of **S1** at 80 °C, catalyzed by **1d** (please refer to the Supporting Information for experimental details).

Information). Indeed, at 80 °C reaction temperature, conversion drops significantly to 34% of the original yield obtained under the same conditions without addition of mercury, whereas the activity of [Au(IPr)(NCMe)]BF_4 remains unchanged. At 34 °C in MeCN, however, the activity of **1d** drops only to 74% of the original yield in the presence of mercury, suggesting higher catalyst stability under milder conditions (refer to Supporting Information, Table S2).

In order to examine whether the new 1,2,3-triazolylidene catalysts also catalyze substrates other than terminal alkynes, we synthesized 2-(2-phenylethynyl)aniline (**S2**) as the starting material for hydroamination of an internal alkyne (Scheme 5).[29] The reaction was complete within 24 h under mild

Scheme 5. Au-Catalyzed Hydroamination of Internal Alkyne Substrate S2



conditions (1 mol % of **1d**, 34 °C) in acetonitrile (monitored via NMR spectroscopy). Again, slight formation of Au colloids was observed. Interestingly, the transformation was complete much more quickly in CD_2Cl_2 at room temperature (about 5 min at room temperature). However, also immediately heavy precipitation of elemental Au was observed, which indicated that the reaction is also easily catalyzed by (undefined) Au nanoparticles.

CONCLUSION

With newly synthesized 1,2,3-triazolylidene Au−Cl complexes as starting materials, a selection of Au precatalysts was isolated and characterized. Most isolated compounds show good stability in air or in wet organic solvents at room temperature for at least 1 day. On the basis of the described observations in hydroamination catalysis, it seems that the newly isolated catalyst systems exhibit limited stability at higher reaction temperatures in comparison to the more common imidazolylidene systems. Under mild conditions, some of the synthesized triazolylidene Au catalysts perform nearly as well as the renowned IPr-based Au systems. As can be deduced from mercury catalyst poisoning experiments, the most stable "normal" 1,2,3-triazolylidene catalyst, **1d**, shows good stability under mild conditions but is less stable at higher reaction temperatures in comparison to [Au(IPr)(NCMe)]BF_4. As shown for "abnormal" 1,2,3-triazolylidenes by others,[11g,30] substitution of the alkyl substituent at the N1 position should certainly improve stability in the systems described here. Furthermore, all tested NHC-based systems show inferior catalytic performance in comparison to (undefined) Au nanoparticles. When focusing on defined molecular homogeneous catalysts, however, improved ligand design seems necessary to leverage the viability of "normal" 1,2,3-triazolylidenes as effective ligands in catalysis and is currently under investigation in our laboratories.

EXPERIMENTAL SECTION

General Information. All described manipulations were carried out under an argon atmosphere by applying standard Schlenk techniques or in a glovebox. Prior to use, glassware was dried at 80 °C overnight and flame-dried in vacuo. Wilmad NMR tubes with Teflon seals were used for catalytic examinations. In order to ensure that the NMR tubes utilized for catalytic examinations did not contain any traces of metal, these were cleaned with aqua regia between catalytic experiments. An MBraun MB SPS solvent purification system was used to obtain dry solvents. These were further degassed by freeze−pump−thaw cycles. Commercially available compounds were used as received. Following literature procedures,[16] 1-methyl-2-phenyl-4-*p*-tolyl-1,2,3-triazolium chloride and 1-cyclohexyl-2-phenyl-4-*p*-tolyl-1,2,3-triazolium chloride were prepared, as well as substrates **S1**[31] and **S2**.[32] ^1H and ^{13}C NMR spectroscopy was performed on a 400 MHz Bruker Avance DPX or a 400 MHz Bruker Avance III spectrometer at 298 K. Residual solvent shifts of the deuterated solvents were used as internal standards for calibration of spectra. Chemical shifts were referenced relative to TMS in parts per million (ppm). Abbreviations used for signal multiplicities: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br). A Varian 670 FT-IR spectrometer was used to conduct IR measurements. Elemental analyses were performed by the microanalytical laboratory of the TUM.

Single-Crystal X-ray Structure Determinations. **2a**: yellow fragment, $C_{21}H_{23}AuClN_3$, M_r = 549.84, orthorhombic, space group *Pbca* (No. 61), a = 9.7218(6) Å, b = 17.9719(11) Å, c = 22.2856(13) Å, V = 3893.7(4) Å^3, Z = 8, λ(Mo Kα) = 0.71073 Å, μ = 7.703 mm^{-1}, ρ_{calcd} = 1.876 g cm^{-3}, T = 123(1) K, F(000) = 2128, θ_{max} = 25.36°, R1 = 0.0157 (2905 observed data), wR2 = 0.0272 (all 3460 data), GOF = 1.02, 236 parameters, $\Delta\rho_{max/min}$ = 0.413/−0.457 e Å^{-3}. **1c**: colorless plate, $C_{18}H_{18}AuN_3O_2$, M_r = 505.32, orthorhombic, space group *Pbca* (No. 61), a = 7.3069(1) Å, b = 19.8442(3) Å, c = 23.0312(3) Å, V = 3339.52(8) Å^3, Z = 8, λ(Mo Kα) = 0.71073 Å, μ = 8.826 mm^{-1}, ρ_{calcd} = 2.010 g cm^{-3}, T = 123(1) K, F(000) = 1936, θ_{max} = 25.36°, R1 = 0.0167 (2556 observed data), wR2 = 0.0322 (all 3064 data), GOF = 1.031, 220 parameters, $\Delta\rho_{max/min}$ = 0.458/−0.401 e Å^{-3}. **1f**: pale yellow fragment, $C_{32}H_{30}AuN_6F_6Sb$, M_r = 931.35, triclinic, space group $P\bar{1}$ (No. 2), a = 11.6548(4) Å, b = 11.9418(4) Å, c = 13.7014(5) Å, α = 97.381(2)°, β = 108.494(1)°, γ = 114.191(1)°, V = 1574.32(10) Å^3, Z = 2, λ(Mo Kα) = 0.71073 Å, μ = 5.581 mm^{-1}, ρ_{calcd} = 1.965 g cm^{-3}, T = 123(1) K, F(000) = 896, θ_{max} = 25.41°, R1 = 0.0139 (5719 observed data), wR2 = 0.0361 (all 5806 data), GOF = 1.123, 419 parameters, $\Delta\rho_{max/min}$ = 0.610/−0.485 e Å^{-3}.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-923626 (**2a**), CCDC-923624 (**1c**), and CCDC-923625 (**1f**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Preparation of (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidenyl)gold(I) Chloride (1a). Under an argon atmosphere, 20 mL of anhydrous dichloromethane were added to a Schlenk tube

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charged with 1-methyl-2-phenyl-4-*p*-tolyl-1,2,3-triazolium chloride (0.500 g, 1.75 mmol, 1.00 equiv) and silver(I) oxide (0.203 g, 0.880 mmol, 0.50 equiv). The reaction solution was stirred at room temperature under exclusion of light for 2 h. Subsequently, the reaction mixture was filtered through Celite. All volatiles of the filtrate were removed under vacuum to give a white precipitate. Then, the white solid was dissolved in 5 mL of anhydrous dichloromethane and [(SMe_2)AuCl] (0.309 g, 0.105 mmol, 0.60 equiv) was added. The reaction mixture was stirred for 2 h under exclusion of light at room temperature. The obtained pale yellow solution was filtered through Celite, and diethyl ether was added to the filtrate to give **1a** as a white solid (0.495 g, 58.7%).

The obtained data agree with literature values.[12]

Preparation of (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidenyl)gold(I) Phenylacetylide (1b). Under an argon atmosphere, 8 mL of anhydrous methanol were added to a Schlenk tube charged with potassium *tert*-butoxide (0.049 g, 0.441 mmol, 2.10 equiv) and phenylacetylene (0.045 g, 0.441 mmol, 2.10 equiv). After 20 min of stirring, **1a** (0.100 g, 0.207 mmol, 1.00 equiv) was added to the clear solution. The reaction mixture was stirred for 16 h at room temperature to afford a white precipitate. The white solid was filtered and washed with water, methanol, and diethyl ether (15 mL each). Thereafter the solid was dried under vacuum to give the product as a white powder (0.951 g, 83.7%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.33 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_{ar}), 7.72−7.61 (m, 3H, CH_{ar}), 7.59−7.47 (m, 4H, CH_{ar} and $H_{phenylacetylide}$), 7.35−7.12 (m, 6H, CH_{ar} and $H_{phenylacetylide}$), 4.27 (s, 3H, NCH_3), 2.39 (s, 3H, CCH_3). ^{13}C NMR (101 MHz, THF-d_6): δ (ppm) = 180.11 (Au-C_{trz}), 157.23 (C_{trz}), 140.04 (C_{ar}), 137.03 (C_{ar}), 133.08 (Au-*C*Ph), 132.65, 132.46, 130.97, 130.20, 129.16, 129.14, 128.52, 127.88, 127.68, 125.89 (all C_{ar}), 103.77 (Au−*C*Ph), 42.00 (NCH_3), 21.56 (CCH_3). MS (FAB) *m*/*z* (%): 547.4 [M]$^+$ (47), 445.5 [M − phenylacetylene]$^+$ (34). MS (ESI) *m*/*z* (%): 993.2 [2M − phenylacetylene]$^+$ (100). Anal. Calcd for $C_{24}H_{20}AuN_3$ (547.13): C, 52.66; H, 3.68; N, 7.68; Au, 35.98. Found: C, 53.01; H, 3.86; N, 7.30; Au, 36.0.

Preparation of (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidenyl)gold(I) Acetate (1c). Under an argon atmosphere, 10 mL of anhydrous dichloromethane were added to a Schlenk tube charged with **1a** (0.100 g, 0.207 mmol, 1.00 equiv). At −78 °C, the solution was transferred to another Schlenk tube containing silver acetate (0.042 g, 0.249 mmol, 1.20 equiv) in 3 mL of anhydrous dichloromethane. The reaction solution was stirred under exclusion of light and was slowly warmed from −78 °C to room temperature within 2 h. Then the reaction mixture was filtered through Celite and the filtrate was concentrated. 10 mL of anhydrous hexane were added to give a product as a white solid (48.3 mg, 56.3%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.35 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH_{ar}), 7.78−7.63 (m, 3H, CH_{ar}), 7.60−7.50 (m, 2H, CH_{ar}), 7.31 (d, $^3J_{HH}$ = 7.8 Hz, 2H, CH_{ar}), 4.24 (s, 3H, NCH_3), 2.40 (s, 3H, CCH_3), 1.96 (s, 3H, $C(O)CH_3$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) 176.89 (Au-C_{trz}), 157.38 ($C(O)CH_3$), 156.16 (C_{trz}), 140.61, 135.72, 132.69, 130.95, 130.05, 127.64, 127.47, 126.91 (all C_{ar}), 42.31 (NCH_3), 24.17 ($C(O)CH_3$), 21.69 (CCH_3). MS (FAB) *m*/*z* (%): 445.5 [M − acetate]$^+$ (48). MS (ESI) *m*/*z* (%): 446.2 [M − acetate]$^+$ (5). Anal. Calcd for $C_{18}H_{18}AuN_3O_2$ (505.11): C, 42.78; H, 3.59; N, 8.32. Found: C, 42.65; H, 3.64; N, 8.20.

Preparation of (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidenyl)gold(I) Bis(trifluoromethanesulfonyl)imidate (1d). Under an argon atmosphere, 10 mL of anhydrous dichloromethane were added to a Schlenk tube charged with **1a** (0.105 g, 0.218 mmol, 1.00 equiv) and silver bis(trifluoromethanesulfonyl)imide (0.089 g, 0.229 mmol, 1.05 equiv). The reaction mixture was stirred at room temperature under exclusion of light for 5 min. Then the reaction mixture was filtered through Celite and all volatiles of the filtrate were evaporated under vacuum. An off-white solid (0.094 g, 67.8%) was obtained as product.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.28 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_{ar}), 7.81−7.65 (m, 3H, CH_{ar}), 7.58−7.48 (m, 2H, CH_{ar}), 7.30 (d, $^3J_{HH}$ = 7.9 Hz, 2H, CH_{ar}), 4.23 (s, 3H, NCH_3), 2.42 (s, 3H, CCH_3). ^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) 156.12 (Au-C_{trz}), 141.20 (C_{trz}), 135.37, 133.12, 131.13, 130.17, 127.46, 126.89, 126.70 (all C_{ar}), 119.97 (q, $^1J_{CF}$ = 323.0 Hz, SCF_3), 42.54 (NCH_3), 21.70 (CCH_3). MS (FAB) *m*/*z* (%): 727.2 [M]$^+$ (3), 695.4 [M − NTf_2 + Trz]$^+$ (100), 446.2 [M − NTf_2]$^+$ (66). MS (ESI) *m*/*z* (%): 695.2 [M − NTf_2 + Trz]$^+$ (88), 487.1 [M − NTf_2 + MeCN]$^+$ (100), 279.2 [NTf_2]$^+$ (9). Anal. Calcd for $C_{18}H_{15}AuF_6N_4O_4S_2$ (726.01): C, 29.76; H, 2.08; N, 7.71; S, 8.83. Found: C, 29.93; H, 2.23; N, 7.70; S, 8.82.

Preparation of (1-Methyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidenyl)gold(I) Acetonitrile Hexafluoroantimonate (1e). Under an argon atmosphere, 8 mL of anhydrous acetonitrile were added to a Schlenk tube to dissolve silver hexafluoroantimonate (0.056 g, 0.166 mmol, 1.05 equiv). The solution was transferred through cannula to another Schlenk tube charged with **1a** (0.076 g, 0.158 mmol, 1.00 equiv) in 2 mL of anhydrous acetonitrile. After stirring for 1 min, the reaction mixture was filtered through Celite. Removal of all the volatiles gave an off-white solid (62.1 mg, 62.1%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.12 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_{ar}), 7.82−7.67 (m, 3H, CH_{ar}), 7.62−7.54 (m, 2H, CH_{ar}), 7.34 (d, $^3J_{HH}$ = 7.8 Hz, 2H, CH_{ar}), 4.26 (s, 3H, NCH_3), 2.49 (s, 3H, CCH_3), 2.43 (s, 3H. ^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) = 156.66 (Au-C_{trz}), 155.24 (C_{trz}), 141.30, 135.13, 133.28, 131.15, 130.31, 127.61, 126.92, 126.77 (all C_{ar}), 120.74 (Au−NCC), 42.69 (NCH_3), 21.72 (CCH_3), 3.46 ($NCCH_3$). MS (FAB) *m*/*z* (%): 486.4 [M − SbF_6]$^+$ (20), 445.5 [M − SbF_6 − MeCN]$^+$ (100). MS (ESI$^+$) *m*/*z* (%): 487.1 [M − SbF_6]$^+$ (100). MS (ESI$^-$) *m*/*z* (%): 235.2 [SbF_6]$^-$ (100). Anal. Calcd for $C_{18}H_{18}AuF_6N_4Sb$ (722.01): C, 29.90; H, 2.51; N, 7.75. Found: C, 30.28; H, 2.75; N, 7.51.

Preparation of (1-Cyclohexyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidenyl)gold(I) Chloride (2a). Under an argon atmosphere, a mixture of 10 mL of anhydrous dichloromethane and 10 mL of anhydrous acetonitrile was added to a Schlenk tube charged with 1-cyclohexyl-2-phenyl-4-*p*-tolyl-1,2,3-triazolium chloride (0.200 g, 0.628 mmol, 1.00 equiv), silver(I) oxide (0.218 g, 0.942 mmol, 1.50 equiv), and 3 Å molecular sieves. The reaction solution was stirred at room temperature under exclusion of light for 18 h. Subsequently, the mixture was filtered through Celite to another Schlenk tube charged with [(SMe_2)AuCl] (0.111 g, 0.377 mmol, 0.60 equiv). After 2 h of stirring under exclusion of light at room temperature, the obtained yellow solution was filtered through Celite and the filtrate was concentrated. Diethyl ether was then added to precipitate the product as an off-white solid. The solid was dried in vacuo (0.120 g, 34.8%).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.33 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_{ar}), 7.82−7.64 (m, 3H, CH_{ar}), 7.46 (dt, $^3J_{HH}$ = 6.9, 1.5 Hz, 2H, CH_{ar}), 7.27 (d, $^3J_{HH}$ = 8.2 Hz, 2H, CH_{ar}), 4.40 (tt, $^3J_{HH}$ = 12.1, 3.8 Hz, 1H, NC*H*), 3.23−2.93 (m, 2H, CCH_2), 2.39 (s, 3H, CCH_3), 2.11−1.83 (m, 4H, CCH_2), 1.66 (d, $^3J_{HH}$ = 13.5 Hz, 1H, CCH_2), 1.50−1.31 (m, 1H, CCH_2), 1.31−1.04 (m, 1H, CCH_2). ^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) 158.19 (Au-C_{trz}), 156.64 (C_{trz}), 140.42, 135.43, 132.90, 131.06, 129.99, 128.06, 127.77, 127.47 (all C_{ar}), 63.43 (NCH), 34.54 (CCH_2), 26.23 (CCH_2), 25.10 (CCH_2), 21.68 (CCH_3). MS (FAB) *m*/*z* (%): 513.5 [M − Cl]$^+$ (100). MS (ESI) *m*/*z* (%): 513.5 [M − Cl]$^+$ (100). Anal. Calcd for $C_{21}H_{23}AuClN_3$ (549.12): C, 45.87; H, 4.22; N, 7.64. Found: C, 46.05; H, 4.24; N, 7.40.

Preparation of (1-Cyclohexyl-2-phenyl-4-tolyl-1,2,3-triazol-5-ylidenyl)gold(I) Acetonitrile Hexafluoroantimonate (2b). Under an argon atmosphere, 8 mL of anhydrous acetonitrile were added to a Schlenk tube to dissolve silver hexafluoroantimonate (0.064 g, 0.190 mmol, 1.05 equiv). Then, the solution was transferred through a cannula to another Schlenk tube charged with **2a** (0.100 g, 0.181 mmol, 1.00 equiv) in 2 mL of anhydrous acetonitrile. After it was stirred for 5 min, the reaction mixture was filtered through Celite. Removal of all the volatiles gave an off-white solid (0.086 g, 60.0%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.12 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH_{ar}), 7.88−7.70 (m, 3H, CH_{ar}), 7.56−7.47 (m, 2H, CH_{ar}), 7.35 (d, $^3J_{HH}$ = 7.9 Hz, 2H, CH_{ar}), 4.52 (tt, $^3J_{HH}$ = 12.1, 3.8 Hz, 1H, NC*H*), 2.66 (pseudo-td, $^2J_{HH}$ = 12.3, $^3J_{HH}$ = 3.4 Hz, 2H, CCH_2), 2.52 (s, 3H, $NCCH_3$), 2.43 (s, 3H, CCH_3), 2.19−2.08 (m, 2H, CCH_2), 2.04−1.91 (m, 2H, CCH_2), 1.48−1.19 (m, 4H, CCH_2). ^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) 157.33 (Au-C_{trz}), 149.33 (C_{trz}), 141.20, 134.79, 133.55, 131.35, 130.32, 127.83, 127.41, 127.29 (all C_{ar}), 121.10 (Au−

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NCC), 63.79 (NCH), 35.39 (CCH_2), 26.12 (CCH_2), 25.04 (CCH_2), 21.71 (CCH_3), 3.52 (Au-NCCH_3). MS (FAB) *m/z* (%): 555.3 $[M - SbF_6]^+$ (7), 514.3 $[M - SbF_6 - MeCN]^+$ (16), 315.1 $[Trz]^+$ (12). MS (ESI) *m/z* (%): 555.1 $[M - SbF_6]^+$ (34), 514.1 $[M - SbF_6 - MeCN]^+$ (3), 235.2 $[SbF_6]^-$ (2).

Procedures for Catalytic Examinations. Typical Catalytic Procedure for Hydroamination of 4-Pentyn-1-amine (S1). In a glovebox, a solution of **S1** (34.5 mg, 414 μmol) and 1,3,5-trimethoxybenzene (20 mg, 119 μmol, used as standard) in 0.9 mL of DCM-d_2 was prepared in a scintillation vial. Furthermore, a catalyst solution of 3 mg of **1e** (4.14 μmol) in 0.9 mL of DCM-d_2 was prepared in another scintillation vial. Portions (0.3 mL) of each solution were quickly added to a Wilmad NMR tube with a Teflon seal (so that the tube contained 138 μmol of **S1**, 49.6 μmol of standard, and 1.38 μmol of **1e**). The NMR tube was quickly sealed and transferred out of the glovebox, and the reaction solution was immediately cooled to −78 °C until measurement of the starting ^{1}H NMR spectrum. After measurement, the NMR tube was quickly heated to 34 °C in an oil bath and left there for 24 h. After 24 h of heating, another ^{1}H NMR spectrum was measured to allow evaluation of conversion of **S1**.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and CIF files giving spectra of all new compounds as well as detailed descriptions of buried volume calculations, computational details, and specific crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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